

Radiation Initiated Synthesis of 2-Acrylamidoglycolic Acid Grafted Carboxymethyl Cellulose as pH-sensitive Hydrogel

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Abstract

This paper exploited a new approach for synthesis of carboxymethyl cellulose grafted poly 2-acrylamidoglycolic acid (CMC-g-PAG) superabsorbent copolymer in aqueous solution by a simple one-step using γ -radiation as a crosslinking agent. The reaction parameters affecting the equilibrium swelling, i.e., mass ratio of AG to CMC and irradiation dose were systematically optimized to achieve a superabsorbent hydrogel with a maximum swelling capacity. The structure, crystallinity, thermal stability and surface morphology were characterized by Fourier transform infrared spectroscopy (FT-IR) & elemental analysis, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM), respectively. FTIR proved that the grafting reaction occurred between the hydroxyl group of CMC and PAG chain. The thermal analysis data showed that the grafted polymer is more thermally stable than pure CMC. The swelling behavior at various pH solutions, temperature and various ionic salt solutions (NaCl as monovalent, CaCl_2 as divalent and FeCl_3 as trivalent) was investigated in details. The effect of cationic salt solutions on the swelling had the following order: $\text{Na}^+ > \text{Ca}^{2+} > \text{Fe}^{3+}$. The pH-reversibility was preliminarily investigated with alternating pH between 12 and 2. The results showed that the equilibrium swelling of CMC/PAG was achieved in 70 min. The hydrogel was responsive to the pH and salts; and it also has reversible swelling and deswelling character.

Keywords

Graft Copolymer; Carboxymethyl Cellulose; 2-Acrylamidoglycolic Acid; γ -Radiation

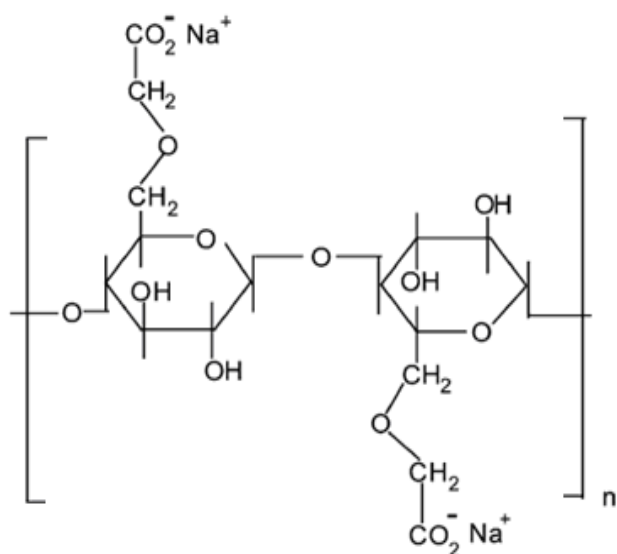
Introduction

A great interest in natural-based superabsorbent

hydrogel has increased recently, mainly due to high hydrophilicity, biocompatibility, nontoxicity, and biodegradability of biopolymers. These materials are characterized with crosslinked macromolecular networks that can absorb water or physical fluids up to many times of their own weight in a short time without dissolution when directly being in contact with the medium [1]. Removal of the absorbed fluids is hard even with applying pressure. According to their excellent characteristics, superabsorbent hydrogels are widely used in many technological and biotechnological fields, such as disposable diapers, feminine napkins, pharmaceuticals, medicals and agricultural & horticultural applications [2–4].

Due to their exceptional properties such as biocompatibility, biodegradability, renewability, and nontoxicity, polysaccharides are used as the core component of the natural-based superabsorbent hydrogels. Carboxymethyl cellulose, an anionic water-soluble polysaccharide, is the most modified cellulose, which can be used in various fields such as detergent, food, paper, and textile industries. CMC is a reaction product of cellulose with sodium hydroxide and chloroacetic acid. It has a number of sodium carboxymethyl groups ($-\text{CH}_2\text{COONa}$), introduced into the cellulose molecule, which promote its water solubility; Scheme 1. Among all the polysaccharides, CMC is easily available, very cheap and has high shear stability. The use of crosslinked CMC, in gel formulations using grafting technique with selected monomers, mainly polyacrylamide, in addition to

other techniques has been reported recently [5–11]. Most of ionic hydrogels usually undergo volume changes in response to a little change in environmental conditions such as heat, pH, electric field, chemical environments, etc. Hydrogels that are sensitive to external stimuli, are often referred to as intelligent and smart hydrogels. They have important applications in the field of medicine, pharmacy, and biotechnology. Among these, pH-sensitive hydrogels have been extensively investigated for the potential use in site-specific delivery of drugs to specific regions of the gastrointestinal tract and have been prepared for the delivery of low molecular weight protein drugs [12,13].



SCHEME 1 STRUCTURE OF CARBOXYMETHYLCELLULOSE.

Although, carboxymethyl cellulose possesses good properties and various industrial applications, it suffers from its drawbacks i.e., biodegradability which limits its uses considerably. For this purpose, 2-acrylamidoglycolic acid has been chosen as a monomer, which is also hydrophilic in nature [14, 15]. 2-Acrylamidoglycolic acid refers to a class of acrylamides containing $-\text{OH}$, $-\text{COOH}$ and $-\text{CONH}-$ functional groups that shows excellent selectivity in separating apatite from siliceous gangue [16]. A number of copolymers have also been recognized to have ability to respond to several stimuli [17] and to recover metal ions [18,19]. Grafting of 2-crylamidoglyconic acid on to polymeric backbone of carboxymethyl cellulose not only improves the drawbacks but also increases its properties such as swelling and flocculation. The improvement is due to the additional properties of both vinyl monomer and carboxymethyl cellulose. The resulting graft copolymer (carboxymethyl cellulose-g-2-acrylamidoglycolic acid) synthesized may be used as absorbent material, coating material due to being

highly thermally stable and flocculent to remove impurities from coal mine waste water.

The present paper reports the modification of carboxymethyl cellulose through the grafting of 2-acrylamidoglycolic acid by free radical polymerization using γ -radiation for further enhancing the water sorption capacity of this natural polymer. The synthesized graft copolymer may be used as superabsorbent materials.

Experimental Materials

Carboxymethyl cellulose of commercial grade was supplied by El-Nasr Pharmaceutical Chemicals Co., Egypt. 2-Acrylamidoglycolic acid of purity 99%, (Merck, Darmstadt, Germany) was used as received. The other chemicals, such as solvents and inorganic salts, were reagent grade and used without further purification.

Radiation Preparation of CMC/PAG Hydrogels

CMC solutions (2%; 2 g in 100 ml distilled water) were dissolved and mixed with various amounts of AG with different CMC: AG compositions and then exposed to γ - radiation (irradiation dose; 20, 30 and 40 kGy) from a ^{60}Co source. The gels formed were cut into small pieces, air dried at room temperature and stored in sealed containers.

Gel Content

Dried hydrogels were extracted with distilled water for 24 h at 100°C to extract the insoluble parts of the hydrogel. The insoluble parts or gelled parts were taken out and washed with hot distilled water for the removal of the soluble parts and then were dried and weighed. This extraction cycle was repeated until the weight became constant. The gel yield of hydrogel was determined as follows:

$$\text{Gel (\%)} = (W_e / W_d) \times 100 \quad (1)$$

where, W_d and W_e represent the weights of the dry hydrogel and the gelled part after extraction, respectively.

Swelling Studies

Dried hydrogel discs (0.3–0.4 mm thickness, 4-mm diameter) were left to swell in distilled water or phosphate & citrate buffer solutions of desired pH (2–12). Swollen gel removed from the swelling medium at regular time intervals and superficially dried with filter paper, then, it was weighed and placed in the same bath. The measurements were continued until a

constant weight was reached.

$$\text{Swelling \%} = (W_s - W_d / W_d) \times 100 \quad (2)$$

where, W_s and W_d represent the weights of swollen and dry samples, respectively. To study the kinetic of water sorption mechanism; the water-intake process was monitored by the determination of the swelling ratio of the hydrogel at desired time intervals as previously described.

Evaluation of Stimuli-Response Character

Individual solutions with acidic and basic values of pH were prepared by dilution of HCl (pH 2) and NaOH (pH 12.0) solutions to achieve $\text{pH} < 6.0$ and $\text{pH} > 6.0$, respectively, then, the pH values (2–12) were precisely determined by using a Jenway 3310 pH Meter. The equilibrium swelling in each pH solution was determined by a method similar to that in distilled water. The pH-responsive behavior was investigated in terms of its swelling and deswelling in each media. Typically, the sample particle (0.1 g) was placed in a pH 12 solutions until equilibrium was reached. Then, the swollen samples were immersed entirely in pH 2 solutions for set time intervals. The swollen samples were filtered, weighed, and the swelling capacity of hydrogel at a given moment was calculated according to the mass change of samples before and after swelling. The same procedure was repeated for three cycles. After every measurement, each solution was renewed. The equilibrium swelling of superabsorbent hydrogel at salt solutions was determined in 0.01–0.15 mol/L NaCl, CaCl_2 and FeCl_3 .

Elemental Analysis

The elemental analysis of CMC and all the graft CMC/PAG compositions was performed using a Carlo Erba 1108 Elemental Analyzer. The estimation of only three elements, that is, carbon, hydrogen and nitrogen was undertaken.

Thermal Gravimetric Analysis (TGA)

Shimadzu TGA-50 system in nitrogen atmosphere (20 ml/min) was used. The temperature range was from the ambient temperature to 500°C at a heating rate of $10^\circ\text{C}/\text{min}$.

Scanning Electron Microscopy (SEM)

The lyophilized dried hydrogels were examined with a Jeol JSM-5400 SEM microscope. The surfaces of the polymers were sputter coated with gold for 3 min.

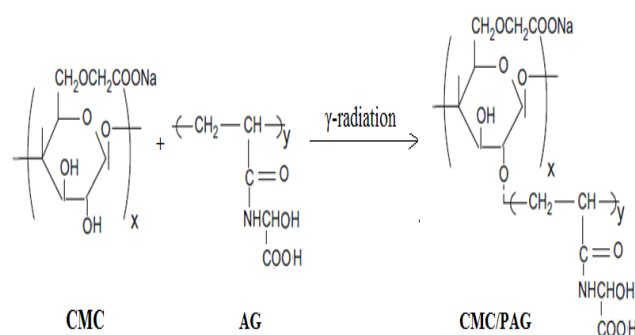
X-ray Diffraction (XRD)

XRD patterns were obtained with Shimadzu XD-DI series apparatus with a nickel-filtered Cu Ka target.

Results and Discussion

Synthesis of CMC/PAG Graft Copolymer

The copolymerization mechanism of synthetic vinyl monomer grafting onto polysaccharides, using γ -radiation as the initiator, has been well studied [20]. Under using radiation, free radicals are formed. The hydrogen radical is abstracted from the hydroxyl group of the polysaccharide to form alkoxy radicals on the substrate. Therefore, this saccharide redox system results in active centers on the substrate, which initiates a radical polymerization of acrylamidoglycolic acid and leads to a graft copolymer. CMC/PAG graft copolymer, with different compositions and varied crosslinking degrees as well as irradiation doses, has been prepared and characterized for further applications such as drug delivery systems, hygiene products, agriculture and horticulture. Scheme 2 shows the synthesis details of the graft copolymers based on carboxymethyl cellulose and acrylamidoglycolic acid by using γ -radiation.



SCHEME 2 CHEMICAL REACTION OF SYNTHESIZING CMC-g-PAG SUPERABSORBENT HYDROGEL BY USING RADIATION

Elemental Analysis

The results of elemental analysis of CMC and different CMC/PAG graft compositions are given in Table 1. CMC does not show any significant presence of nitrogen. However, the negligible amount of nitrogen may be because of the trace quantities of unisolated proteins in the polysaccharides. It has been found that there is a considerable percentage of nitrogen in the graft copolymers, which is accounted for the presence of grafted PAG chains. In the series of graft copolymers based on CMC, the variation in the nitrogen content, although not much, is significant in case of CMC-g-PAG. The higher percentage of

nitrogen may be due to the increased PAG content in the graft copolymer, which is also due to the higher moles of acrylamidoglycolic acid in the reaction feed. Among other graft compositions, CMC:AG (50:50 wt%) has the smallest percentage of nitrogen, which has the lowest polyacrylamide content compared to the CMC:AG composition at 10:90 wt% which has the highest nitrogen content.

TABLE 1 ELEMENTAL ANALYSIS OF CMC AND DIFFERENT CMC: AG COMPOSITIONS OF CMC/PAG GRAFT COPOLYMERS.

| CMC: AG composition | Carbon (%) | Hydrogen (%) | Nitrogen |
|---------------------|------------|--------------|----------|
| 100 : 0.0 | 32.4 | 5.7 | 0.08 |
| 50 : 50 | 52.4 | 7.5 | 14.8 |
| 30 : 70 | 46.6 | 6.9 | 15.5 |
| 20 : 80 | 44.7 | 6.7 | 16.1 |
| 10 : 90 | 42.9 | 6.8 | 16.9 |

FTIR Spectroscopy

The IR spectra of CMC, PAG, and CMC-g-PAG are shown in Fig. 1a–c, respectively. From the IR spectra of CMC (Fig. 1a), it showed a broad absorption band at 3444 cm^{-1} , due to the stretching frequency of the -OH group. The band at 2921 cm^{-1} was due to C-H stretching vibration. Appearance of a strong absorption band at 1618 cm^{-1} was due to the presence of COO groups. The bands around 1423 and 1326 cm^{-1} were assigned to CH_2 scissoring and -OH bending vibration, respectively. The band at 1061 cm^{-1} is due to CH-O-CH_2 stretching [21]. In the case of PAG (Fig. 1b), a broad absorption band at 3431 cm^{-1} was for the N-H stretching frequency of the NH_2 group. Two strong bands around 1689 and 1647 cm^{-1} were due to amide-I (C=O stretching) and amide-II (NH bending), respectively. The bands around 1400 and 2922 cm^{-1} were for the C-N and C-H stretching vibrations, respectively. Other bands at 1458 and 1323 cm^{-1} were attributed to CH_2 scissoring and CH_2 twisting [22]. For IR spectrum of CMC-g-PAG (Fig. 1c), the presence of a broad absorption band at 3434 cm^{-1} was due to the overlap of -OH stretching band of CMC and -NH stretching band of PAG. A band at 1652 cm^{-1} was due to amide-I (C=O stretching) of the amide group of PAG and the band at 1618 cm^{-1} of CMC and amide-II band of PAG overlapped with each other and led to a broad band at 1628 cm^{-1} . The presence of a band at 1733 cm^{-1} was due to free acid groups. The bands around 1404 and 2922 cm^{-1} were for the C-N and C-H stretching vibrations, respectively. Other bands at 1458 and 1338 cm^{-1} were attributed to CH_2 scissoring and CH_2 twisting. Also, there was an important peak at 1068 cm^{-1} which was assigned for the CH-O-CH_2 group

resulting from grafting reaction between the hydroxyl group located in anhydroglucose C_2 position and the p-bond of PAG. The primary peaks existing in the CMC-g-PAG characteristic for the groups of AG, and the shift in the band corresponding to OH group, may suggest formation of ether ($>\text{CH-O-CH}_2$) during the grafting copolymerization. Accordingly, it is apparent that FTIR presented a strong evidence of grafting of PAG branches onto the polysaccharide backbone; (since homopolymers were removed by solvent extraction).

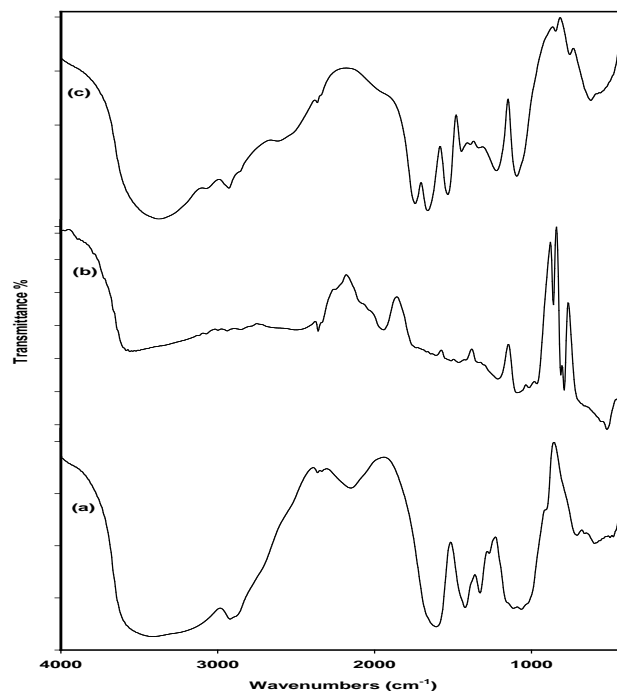


FIG. 1 FTIR SPECTRA OF CMC (a), PAG (b) AND CMC/PAG (c)

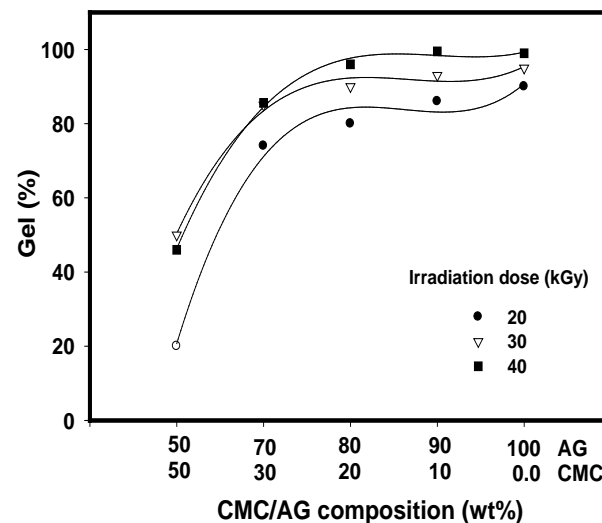


FIG. 2 EFFECT OF CMC: PAG COMPOSITION ON THE GEL (%) OF CMC/PAG SUPERABSORBENT HYDROGEL

Gel Content

Only a few reports on the attempts of crosslinking of

polysaccharides and their derivatives by ionizing radiation have been found in the literature. Polysaccharides have been used as additives to synthetic polymers, in amount of few percents of the overall compounds content, in order to improve properties of the final gel, i.e., to avoid the formation of bubbles in the bulk material and to enhance mechanical properties [23, 24]. There are many factors affecting the polymer gel content among them, polymer compositions and irradiation doses. The effect of various CMC: AG compositions on the gel % of CMC/PAG hydrogel at different irradiation doses was investigated and shown in Fig. 2. It is clear that the gel content as well as crosslinking density of hydrogel increase with increasing of AG content in the polymeric blend feed solutions as well as irradiation dose to reach a maximum value ranging from 90% to 99%.

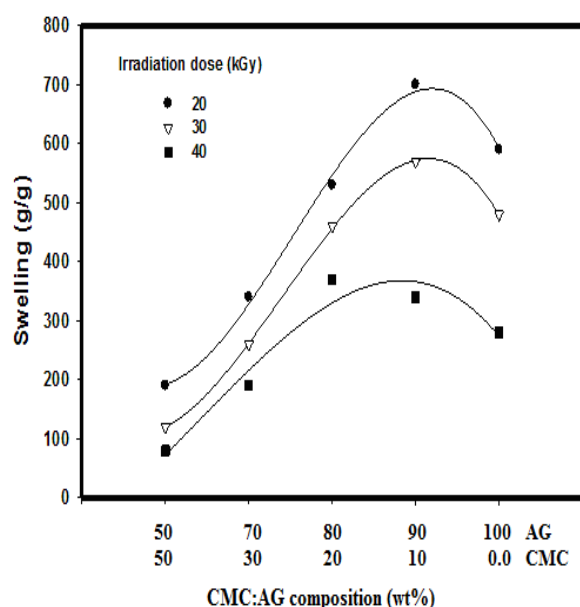


FIG. 3 EFFECT OF CMC:PAG COMPOSITION ON THE EQUILIBRIUM SWELLING CAPACITY OF CMC/PAG SUPERABSORBENT HYDROGEL.

Swelling Studies

1) Effect of Preparation Conditions on CMC/PAG Swelling

Among these preparation conditions, material ratio or composition and irradiation dose have great influence on equilibrium swelling of CMC/PAG hydrogels. The effect of different CMC: AG mass ratios (50:50, 70:30, 80:20, 90:10 and 100:0.0) in the feed mixture and various irradiation doses; 20, 30, 40kGy on equilibrium swelling was showed in Fig.3. It was evident that equilibrium swelling presented a trend of first increase and then

decrease, the highest swelling capacity was obtained at the CMC: AG composition reaching to 90:10 wt%. The increasing swelling capacity with increasing AG content is attributed to the following facts. Since 2-acrylamidoglycolic acid is a hydrophilic monomer, it increases the water absorbing capacity and water retention character of graft copolymer. The long pendant chains of AG are responsible for maximum hydrophilic character in graft copolymer thereby increasing the value of swelling ratio. In other words, as the weight ratio of AG to CMC increases, more AG molecules could be available in the vicinity of the chain propagating sites of CMC macroradicals as well as increase hydrophilic groups such as $-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$, which enhances the hydrophilicity of the corresponding superabsorbent hydrogel, and then the swelling capacity is improved. A similar result has been reported by Pourjavadi et al [25]. In case of pure PAG, the swelling capacity decreased as a result of increased crosslinked chains that were enhanced with increased irradiation doses from 20-40 kGy.

The results were supported by study the morphological properties of CMC/PAG hydrogel by using SEM of CMC, PAG and CMC/PAG at irradiation dose; 20 kGy (Fig. 4). It can be noted that SEM images exhibited undulant, rough and porous structure, which causes an increased surface area of the hydrogel. This kind of surface would facilitate water molecules to diffuse into the polymeric network, and may be of benefit to improving the equilibrium swelling of corresponding superabsorbent hydrogel. Also, the comparison of these figures revealed that grafting has taken place.

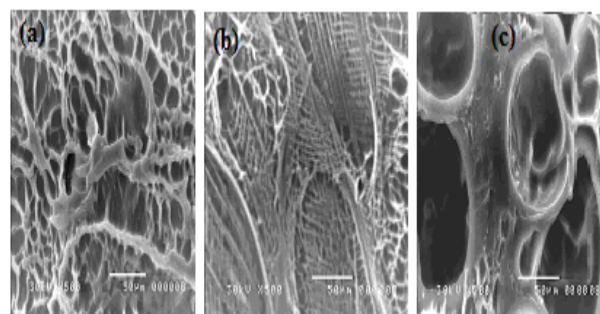


FIG. 4 SCANNING ELECTRON MICROGRAPHS OF (a) CMC, (b) PAG AND (c) CMC/PAG

2) Swelling Kinetics

Fig. 5 shows the swelling kinetic of the optimized superabsorbent hydrogel in distilled water at consecutive time intervals. Initially, the swelling

rate increased sharply within 50 min, then began slowly, and took 70 min to reach equilibrium state, implying that CMC/PAG samples have quite fast swelling rate.

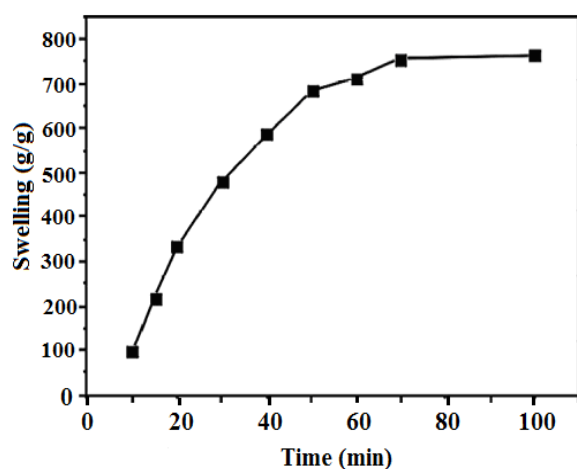


FIG. 5 SWELLING KINETICS OF THE CMC/PAG SUPERABSORBENT HYDROGEL

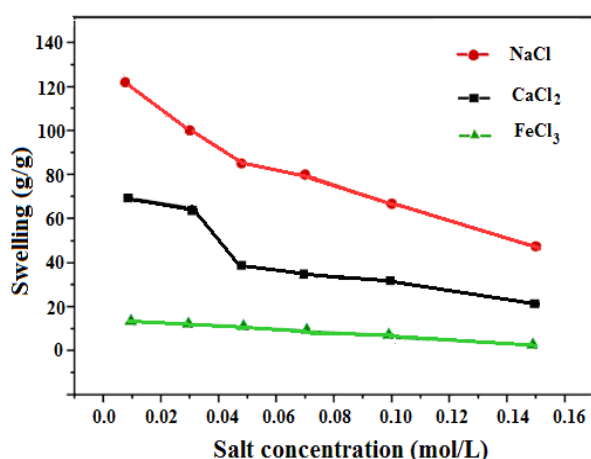


FIG. 6 EQUILIBRIUM SWELLING OF THE OPTIMIZED CMC/PAG SUPERABSORBENT HYDROGEL IN NaCl, CaCl₂ AND FeCl₃ SOLUTIONS

3) Swelling of CMC/PAG Superabsorbent Hydrogel in Various ionic Salt Solutions

Fig. 6 showed that the equilibrium swelling of hydrogel decreased in NaCl, CaCl₂, and FeCl₃ (0.001-0.15 mol/L) solution with the increase of the salt concentration. These results are due to the fact that the osmotic pressure difference between the hydrogel and the external solution is reduced with increasing solution concentration. The charge screening effect (shielding effect) of the cations is another factor that influences the equilibrium swelling in salt solutions. When this effect is operating, the perfect anion-anion repulsive force is prevented by cations [25]. It was concluded that the equilibrium swelling of the hydrogel in the studied

salt solutions from the highest to the lowest is Na⁺ > Ca²⁺ > Fe³⁺ at various salt solution concentrations. This is because Ca²⁺ and Fe³⁺ can form inter and intramolecular complexes with carboxylate groups and hydroxide radical in hydrogels, leading to deswelling or contraction [26]. An additional reason may be the increased electrostatic attraction between anionic sites of chains and multi-valent (Ca²⁺ and Fe³⁺) cations resulting in an increase in the “ionic crosslinking” degree of hydrogel, which became more rigid and subsequent loss of swelling [25].

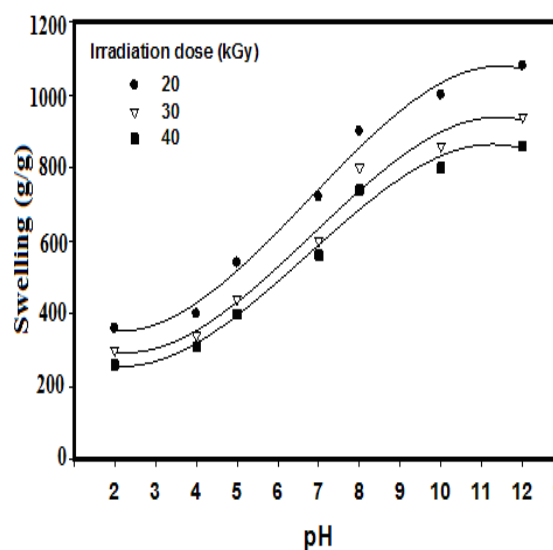


FIG. 7 EFFECT OF pH ON THE EQUILIBRIUM SWELLING CAPACITY OF CMC/PAG SUPERABSORBENT HYDROGEL

4) Effect of pH on Swelling

Superabsorbent hydrogels exhibit swelling changes for a wide range of pH. Therefore, in this series of experiments, equilibrium swelling for the prepared hydrogels, as shown in Fig. 7, was studied at various pH solutions ranged from 2 to 12 and different irradiation doses. It has been reported that the swelling properties of CMC/PAG superabsorbent gels are influenced by the buffer composition and pKa. A progressive increment of swelling was observed with increase of pH from 2 to 12 where a maximum swelling in the range of 850-1100 (g/g) was obtained at irradiation doses from 20-40 kGy, respectively. Such observed sensitivity to pH variation is in agreement with results published by Mohy Eldin et al., in which they studied the effect of pH variation on the swelling of pH-sensitive polyacrylamide-grafted carboxymethyl cellulose hydrogel system composed of acrylamide and carboxymethyl cellulose. These gels exhibited a fair pH-dependent

swelling behavior as the pH of the swelling medium varied from 1.0 to 11 [21]. The minimum swelling in the acidic pH could be explained on the basis of the formation of complex structures within the gel network due to H-bonding interactions between -COOH , -OH and -CONH- groups. These interactions resulted in the formation of a compact or tight structure which did not permit much movement of polymeric segments within the hydrogel network. Also, -COOH groups within the network remained almost nonionized; thus imparting almost non-polyelectrolyte behavior to the gel [27]. In the medium of pH12, the almost complete ionization of -COOH groups resulted in an extensive chain relaxation due to repulsion among similarly charged -COO^- groups present along the macromolecular chains. Moreover, this dissociation also caused an increase in ion osmotic swelling pressure. These two factors were thus responsible for the high degree of swelling in the medium of pH 12.

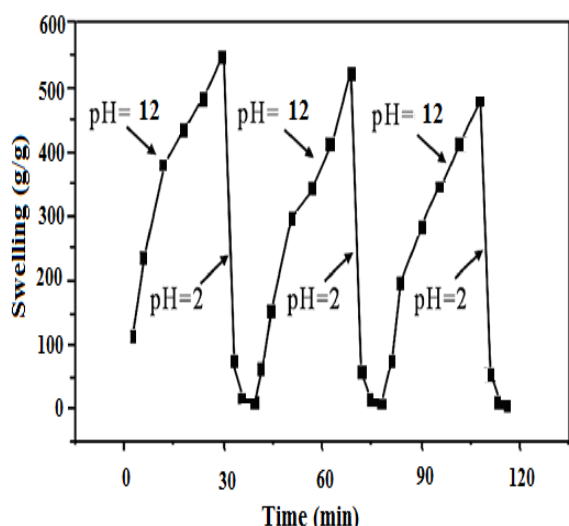


FIG. 8 ON-OFF SWITCHING BEHAVIOR AS REVERSIBLE PULSATILE SWELLING (pH12) AND DESWELLING (pH 2) OF THE OPTIMIZED CMC/PAG SUPERABSORBENT HYDROGEL

5) pH-responsive Behavior of CMC/PAG Hydrogels

Since the CMC/PAG superabsorbent hydrogel shows different swelling behaviors at various pH, so pH-reversibility swelling-deswelling behavior was investigated in the solutions at pH 12 and 2. Fig. 8 shows a stepwise reproducible swelling change of the hydrogel at 25°C with alternating pH between 12 and 2. At pH12, the hydrogel swells up to 550 g H₂O/g gel due to anion-anion repulsive electrostatic forces, while, at pH 2, it shrinks within a few minutes due to protonation of the carboxylate and hydrogen-bonding interaction

between -OH and -COOH groups [25]. After three on-off cycles, the CMC/PAG superabsorbent hydrogel still has better responsive to environmental pH stimulants, suggesting that the CMC/PAG superabsorbent hydrogel possess excellent pH reversibility. Similar on-off switching properties as reversible swelling and deswelling have been reported for other hydrogels [26].

6) Temperature-Responsive Behavior of CMC/ PAG Hydrogels

The influence of temperature on the swelling of CMC/PAG hydrogel which prepared at CMC: AG composition; 90/10 wt% and irradiation dose; 20 kGy was studied in the range 10–60°C and the results are shown in Fig. 9. It indicates that the swelling ratio increases with increasing temperature of the swelling bath. The observed increase may be attributed to the fact that, on raising the temperature both the segmental mobility and diffusion of water molecules increase, which leads to an enhanced swelling of the hydrogel [20].

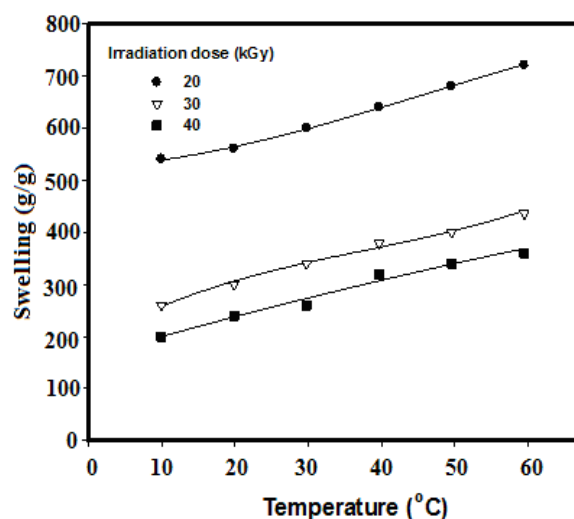


FIG. 9 EFFECT OF TEMPERATURE ON THE EQUILIBRIUM SWELLING CAPACITY OF CMC/PAG SUPERABSORBENT HYDROGE

Thermogravimetric Analysis (TGA)

The TGA curves of CMC, PAG, and CMC-g-PAG in nitrogen atmosphere are shown in Fig. 10. In general, the main decomposition of the polysaccharides (CMC) starts above 250°C. The first stage was attributed to desorption of moisture as hydrogen bound water to the polysaccharide structure. The second and third stages of decomposition took place at 250 and 340°C, respectively, probably due to depolymerization with formation of water, CO, CO₂ and CH₄. [28] As there are

COO⁻ group in the case of CMC, it is decarboxylated in this temperature range. The rate of weight loss is increased with increase in temperature. In case of PAG, the initial weight loss is followed by a continuous weight loss with increasing temperature. The degradation after that is due to the loss of the NH₂ group in the form of ammonia with the formation of imide groups via cyclization [29]. Ammonia and water are the only volatile products below 320°C in PAG. [30]. The pattern of copolymer thermal decomposition, exemplified by CMC-g-PAG, is different from that for the starting materials (CMC and PAG). The graft decomposition was observed in at least four stages. The grafting of PAG chains onto the polysaccharide causes significant change in both CMC and PAG thermal stability, as well enhances the CMC resistance to heat. This can also be proved by the T50 (the temperature at which the half weight loss occurs) which was 300, 350, and 391°C for CMC, PAG, and CMC-g-PAG, respectively. This behavior has been observed for sodium alginate [31] and cashew gum [29]-grafted polyacrylamide.

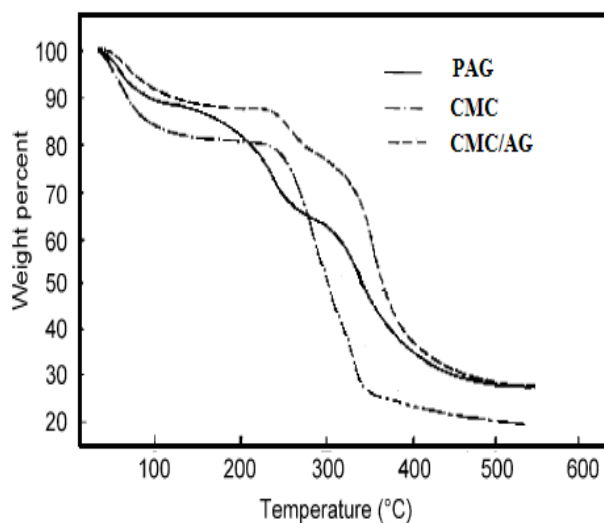


FIG. 10 TGA CURVES OF CMC, PAG, AND CMC-g-PAG.

XRD Analysis

The X-ray diffraction patterns of CMC and CMC/PAG are depicted in Fig. 11a and b, respectively. There is a shift peak at $2\theta = 23^\circ$ in CMC/PAG corresponding to the position at $2\theta = 20^\circ$ observed in CMC pattern. This could be explained by a rearrangement in the morphology of the polymeric chain after grafting of PAG to CMC. Moreover, it is clearly seen that there are two peaks disappearing at the position $2\theta = 33^\circ$ and $2\theta = 45^\circ$ in CMC/PAG contrasted to CMC pattern. These phenomena could be partially explained from the grafting molecular structure of CMC/PAG showed

in Fig. 11b. This indicates the reduction power of H-bonding connection between the grafting cellulosic chains due to the hydroxyl group in anhydroglucose translation into the ether group during the grafting copolymerization [32].

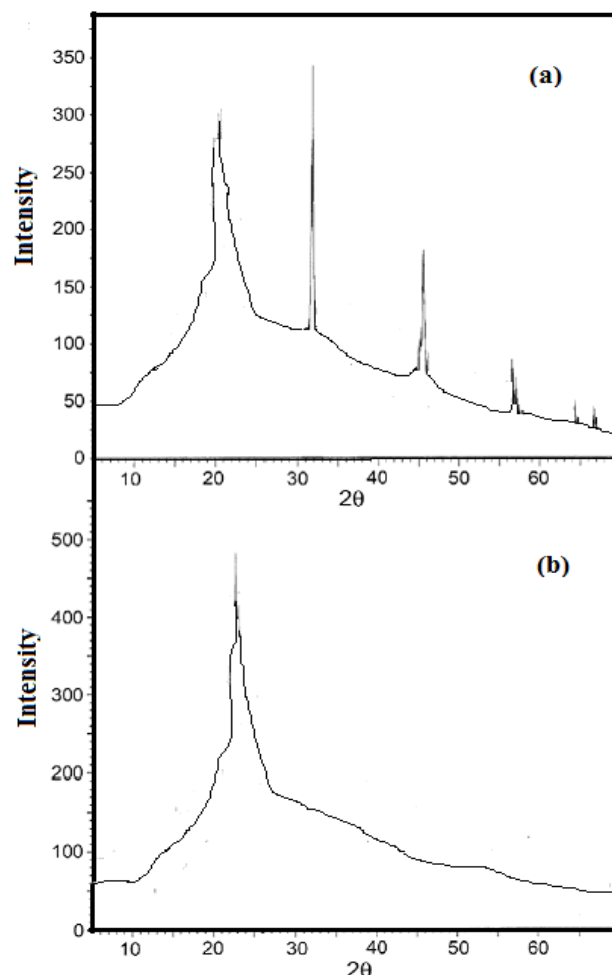


FIG. 11 X-RAY DIFFRACTION PATTERN OF (a) CMC AND (b) CMC/PAG

Conclusions

Poly (2-acrylamidoglycolic acid) was grafted onto carboxymethyl cellulose, via free radical polymerization by using gamma radiation. The synthesized graft copolymer i.e., carboxymethyl cellulose-g-2-acrylamidoglycolic acid shows better results for gel content and swelling behavior. This could be interpreted that graft copolymer shows the enhancement in these properties. The results of IR and XRD indicated that acrylamidoglycolic acid has successfully grafted to the CMC. The spectroscopic data confirmed that the grafting of 2-acrylamidoglycolic acid might have taken place at hydroxyl group of CMC. SEM confirmed a changed morphology to a fibrillar structure. The pH sensitivity was proved; as the grafted polymer attained its

maximum swelling at pH 12 whereas the minimum swelling was observed under acidic conditions; pH 2. The rate of water uptake in the grafted polymer was higher than that of the homopolymer hydrogel. The thermal data show that the synthesized graft copolymer is thermally more stable than pure carboxymethyl cellulose. The maximum equilibrium swelling of the optimized hydrogel in distilled water is about 700 g/g. The equilibrium swelling of the hydrogel in salt solutions from the highest to the lowest is $\text{Na}^+ > \text{Ca}^{2+} > \text{Fe}^{3+}$. Furthermore, swelling capacity of CMC/PAG in various pH solutions as well as swelling-deswelling behavior of the product exhibited high pH-sensitivity and reversible pH-responsiveness properties. All those results suggested that gamma-radiation may provide a new approach for synthesize a water-soluble polymer containing natural polymer; CMC and polymer containing three potential ligand groups; PAG. It may be concluded that superabsorbent CMC/PAG hydrogel can be considered a very promising candidate for drug delivery systems, hygiene products, agriculture and horticulture.

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